

Universal bridge functional for infinitely diluted solutions: a case study for Lennard-Jones spheres of different diameter

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Volodymyr P. Sergiievskyi,
Andrey I. Frolov

Max Planck Institute for Mathematics in the Sciences,
Inselstrasse 22, DE-04103, Leipzig, Germany,
e-mail: sergiiev@mis.mpg.de

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Abstract

In the paper we propose an universal bridge functional for the closure of the Ornstein-Zernike (OZ) equation for the case of infinitely diluted solutions of Lennard-Jones spheres of different size in the Lennard-Jones fluid. Bridge functional is parameterized using the data of the Molecular Dynamics (MD) simulations. We show that for all investigated systems the bridge functional can be efficiently parameterized with the exponential function which depends only on the ratio of sizes of the solute and solvent atoms. To check the parameterization we solve the OZ equation with the closure which includes the parametrized functional and with the closure without the bridge functional (Hyper-netted chain closure). We show that introducing the bridge functional allows to obtain radial distribution functions (RDFs), which are close to the MD results and essentially improve predictions of the location and height of the first peak of the RDF.

Keywords: Ornstein-Zernike equation, Bridge functional, Molecular Dynamics, Lennard-Jones fluid

1 Introduction

Integral Equation Theory Of Liquids (IETL) is an effective instrument for description of structural and thermodynamic properties of solutions. The main equation of IETL is the Ornstein-Zernike integral equation [1], which connects the direct and the total correlation functions of the particles of the system. Another fundamental equation which connects the direct and the total correlation functions is the closure relation [2]. Ornstein-Zernike equation together with the closure relation allows to calculate the particle-to-particle correlation functions of the system which in turn gives an opportunity to calculate the main thermodynamic parameters of the system [3]. For the molecular systems one often uses approximations of the Ornstein-Zernike equation. The most popular of them are the reference interaction site model (RISM) [4, 2] and three-dimensional reference interaction site model (3DRISM) [5, 6]. There were developed efficient numerical algorithms for solving the

RISM and 3DRISM equations [7, 8, 9, 10]. Recently there were proposed number of methods of parameterizing the results of RISM and 3DRISM calculations. These methods allow to predict the free energy of solvation of organic and bioactive molecules with the average error 1 kcal/mol [11, 12, 13, 14, 15, 16].

Ornstein-Zernike, RISM and 3DRISM equations give a qualitatively correct description of the local structure of the liquid. For example, RISM equations can correctly predict asymmetry of ion solvation [17, 18], allow to predict the stability of molecular aggregates in solution [19, 20], and ligand-substrate binding [21, 22]. However, often OZ, RISM and 3DRISM equations cannot reproduce many quantitative parameters such as the radial distribution functions (RDF) or the solvation free energy (SFE) [23, 14, 24].

This is explained by the fact, that the closure relation contains so-called bridge functional which is represented as an infinite sum of integrals of correlation functions and thus is practically in-computable [3]. Usually, to obtain the numerical solution of the equations of IETL one uses the empirical closures. Not all of these closures give the good coincidence with experiments. Several closures were obtained for the simplified models. To name a few: the Hyper Netted Chain (HNC) closure, where the bridge functional is simply ignored, the Percus-Yevick closure [25], the Martynov-Sarkisov closure [26], the Verlet Modified closure [27] and others [28]. Parameterization of the molecular dynamics (MD) simulation data is another perspective method to obtain the bridge functional [29, 30]. In the paper [31] it was proposed to use the closure with the repulsive bridge correction where the atom-atom potentials contained an additional repulsive component. In many cases one performs the bridge parameterization for different parts of the phase diagram, in particular for the density and temperature near the critical point [32, 33]. In the current paper we consider the bridge functional for the two-component systems with the fixed density and temperature of the system. We consider only the case of the infinitely diluted solutions, because such systems are the most often used for the prediction of the thermodynamic properties of biological molecules. In our work we consider the simplified model, where the solvent is a liquid of Lennard-Jones balls which have the σ_{22} parameter coinciding with the σ parameter if the oxygen atom of the SPC/E water model [34] (we denote with the number 1 the solute and with the number 2 the solvent particles). As a solute we use the Lennard-Jones balls with diameters from $0.25\sigma_{22}$ to $2\sigma_{22}$, where σ_{22} is the diameter of the solvent (here and below we call the σ parameter of the LJ potential "the diameter"). The goal of the current paper is building the universal empirical bridge functional which has the good coincidence with the data of the molecular dynamics (MD) simulations. In our work we perform the MD simulations for all of the investigated systems and obtain the radial distribution functions (RDF). By using the OZ equation we obtain the direct correlation functions and by using the closure relation we calculate the bridge functional for each of the systems. We parameterize the bridge functional with the exponential function which includes two empirical parameters and determine the dependency of these parameters on the size of the solvent σ_{11} . In such a way, we obtain the universal formula for the bridge functional for the Lennard-Jones balls of different diameter. At the end we compare the solutions of the Ornstein-Zernike equations with two different closures: hyper-netted-chain (HNC) closure which ignores the bridge functional and the closure which includes the proposed empirical bridge functional. We show that introducing the bridge functional can essentially improve the results of the calculations and make them nearer to the results of the MD simulations. Our main interest is the accurate calculation of the thermodynamical and structural parameters of the aqueous solutions of bioactive compounds by using the IETL. We believe, that introducing the bridge functionals allows in many cases to substitute the computationally expensive MD simulations with the cheaper IETL method, for example for the description of the interaction of osmolites with the nanoobjects and surfaces [35, 36, 37, 38] and

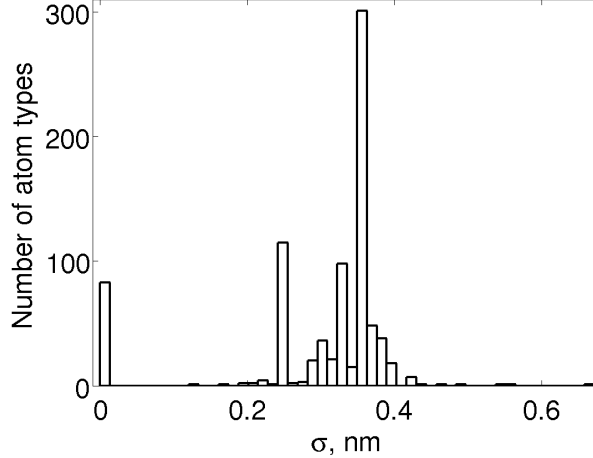


Figure 1: Distribution of σ Lennard-Jones potential parameters of the atoms from the OPLS force-field. The data is obtained from the Gromacs 4.5.3 program package[43] (file oplsaaff/ffnonbonded.itp).

biomolecules [39, 40, 41, 42].

2 Description of the method

2.1 Molecular dynamics simulations

2.1.1 Description of the investigated systems

For the molecular dynamics simulations we used the program package Gromacs 4.5.3 [43]. We created eight systems which contain one particle with the Lennard-Jones (LJ) potential (see the equation (1)) with eight different values of σ_{11} . The particle was solved with infinite dilution in the LJ fluid with the fixed values σ_{22} and ϵ_{22} (these values were the same for all systems). We denote the solute by the digit 1 and the solvent by the digit 2. The solute and the solvent had the same ϵ parameter: ($\epsilon_{11} = \epsilon_{22}$). In our work we simulated the systems with the following values of the σ_{11} parameter: $\sigma_{11} = k \cdot \sigma_{22}$, $k = 0.25, 0.5, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00$. Such range of σ_{11} parameters was used because in the popular OPLS (Optimized Potential for Liquid Simulations) force-field [44] the most of σ parameters lies in the range from $0.25 \sigma_{22}$ to $2 \sigma_{22}$, where $\sigma_{22} = 0.3166$ nm is the LJ parameter if the water oxygen (see Figure 1).

$$u_{ij}^{LJ}(r) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right) \quad (1)$$

where i and j denote the type of particles.

Mixed interaction parameters of the LJ particles of the solute and solvent were calculated using the OPLS methodology:

$$\begin{aligned} \epsilon_{12} &= \sqrt{\epsilon_{11} \cdot \epsilon_{22}} \\ \sigma_{12} &= \sqrt{\sigma_{11} \cdot \sigma_{22}} \end{aligned} \quad (2)$$

Varying the σ_{11} we can determine the influence of the solvent at the infinite dilution in the identical solvent on the structural characteristics (solute-solvent radial distribution function (RDF)) and the shape of the bridge functional.

2.1.2 Thermodynamical parameters, which are used in the simulations

In the current work we are looking for the bridge functional for the following solvent: LJ fluid, temperature $T=300\text{K}$, number density 33.3294 particles/ nm^3 (corresponds to the water density 997.09 g/l), with the LJ parameters which corresponds to the oxygen atom in the SPC/E water model ($\sigma_{22}=0.316557$ nm, $\epsilon_{22}=0.6500194$ kJ/mol) [34]. These parameters in the reduced units are the following: density= 1.0573 particles/ σ_{22}^3 , $T=3.8365$ ϵ_{22} .

2.1.3 Parameters of the molecular dynamics simulations

We used the "leap-frog" scheme [45] for the numerical integration of the equation of motion. Integration step corresponded to the 0.002 ps. Cutoff radius for the LJ potential (r_{cutoff}) was 1.2 nm, while the LJ potential was corrected to be zero at the distance r_{cutoff} :

$$\begin{aligned} u_{ij}(r) &= u_{ij}^{LJ}(r) - u_{ij}^{LJ}(r_{\text{cutoff}}) & , r < r_{\text{cutoff}}, \\ u_{ij}(r) &= 0 & , r \geq r_{\text{cutoff}} \end{aligned} \quad (3)$$

The neighbour list was created using the "cell list" method [46], which is referenced in the Gromacs package as the "grid search" method [45]. The neighbour list was re-newed each tenth step with the cutoff radius 1.4 nm. We performed the simulations in the canonical ensemble (NVT). We used the Berendsen thermostat [47] for preserving the temperature of the system ($T=300\text{K}$) with the parameter $\tau=2$ ps.

2.1.4 Preparing the systems and calculationg the RDF functions

Initially we prepared the cubic cell which contain 4168 solvent LJ particles of size 5.0007 nm^3 using the packmol program [48]. Coordinates of the particles were optimized using the gradient descent method [45]. After that the system was simulated during the 1 ns in the NVT ensemble to establish the equilibrium. In the final configuration one of the solvent atoms was changed to the solute atom (LJ particle with the given σ_{11}). The systems with different solute atoms were optimized using the gradient descent method [45]. After that each of the systems was simulated during the 25 ns to obtain the necessary statistics. Coordinates of the particles were saved each 0.2 ps for the further calculation of the solute-solvent RDF. RDF was calculated using the "g_rdf" tool from the Gromacs 4.5 package.

2.2 Obtaining the bridge functional from the molecular dynamic simulation data

For the bridge functional calculation we used the RDF functions which were obtained from the MD simulations. For the bridge functional calculation two types of RDF were used: solute-solvent RDFs ($g_{12}(r)$) and solvent-solvent RDFs ($g_{22}(r)$). Using these functions the total correlation functions were calculated: $h_{i2}(r) = g_{i2}(r) - 1, i = 1, 2$. To calculate the bridge functional one also needs to know the solute-solvent direct correlation functions $c_{12}(r)$. We used the Ornstein-Zernike equation [1, 3] to obtain these functions:

$$\hat{c}_{12}(k) = \frac{\hat{h}_{12}(k)}{1 + \rho \hat{h}_{22}(k)} \quad (4)$$

where ρ is the solvent number density (number of solvent of particles in the unit volume), $\hat{c}_{12}(k)$, $\hat{h}_{12}(k)$, $\hat{h}_{22}(k)$ are the Fourier-Bessel transforms of the functions $c_{12}(r)$, $h_{12}(r)$, $h_{22}(r)$ correspondingly. The Fourier-Bessel transform of the total correlation functions $h_{ij}(r)$ is given by the following formula [49]:

$$\hat{h}_{ij}(k) = \mathcal{F}[h_{ij}(r)] = \frac{4\pi}{k} \int_0^\infty h_{ij}(r) r \sin(kr) dr \quad (5)$$

The Fourier-Bessel transform on the discrete grid can produce artefacts which are seen as some oscillations of the $\hat{h}_{ij}(k)$ function near the $k = 0$. In the current work these artefacts were removed by the following method: For each pair of the neighbouring local minimum and maximum points k_{\min} and k_{\max} of the high-frequency oscillations the value in the point $\frac{1}{2}(k_{\min} + k_{\max})$ was taken to be equal to the mean value in the extramum points: $\hat{h}_{ij}(\frac{1}{2}(k_{\min} + k_{\max})) = \frac{1}{2}(\hat{h}_{ij}(k_{\min}) + \hat{h}_{ij}(k_{\max}))$, and afterwards the function was interpolated in the vicinity of $k = 0$ using the cubic splines basing on these mean values (see fig:denoise ??).

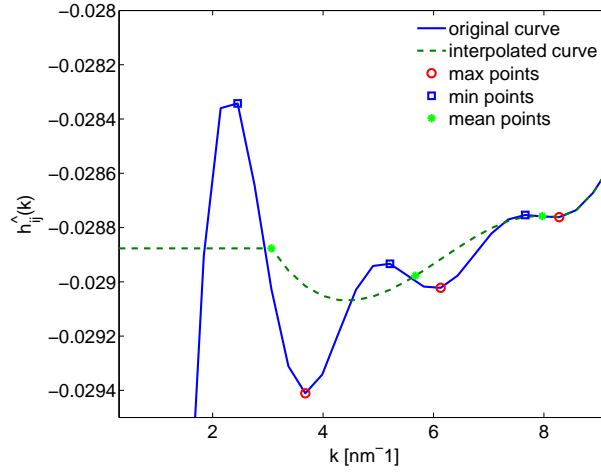


Figure 2: Removing the high-frequency oscillations of the functions $\hat{h}_{ij}(k)$ in the vicinity of $k = 0$. In the picture is presented the function for $\sigma_{11}=\sigma_{22}$.

The $c_{12}(r)$ can be restored from its Fourier image using the inverse Fourier-Bessel transform [49]:

$$c_{12}(r) = \mathcal{F}^{-1}[\hat{c}_{12}(k)] = \frac{1}{2\pi^2 r} \int_0^\infty \hat{c}_{12}(k) k \sin(kr) dk \quad (6)$$

The bridge functional $B_{12}(r)$ can be obtained from the closure relation using the following formula:

$$B_{12}(r) = \ln g_{12}(r) + \beta U_{12}(r) - g_{12}(r) + c_{12}(r) + 1 \quad (7)$$

Bridge functionals for the different solute/solvent size ratios are given in Figure 3. Dispite the quite complicated shape of the bridge functionals in the first approximation they can be sufficiently good approximated with the exponential function $B_{12}(a_1, a_2, r)$ with two fitting parameters a_1 and a_2 :

$$B_{12}(a_1, a_2, r) = -a_1 \exp(-a_2(r - r_0)) \quad (8)$$

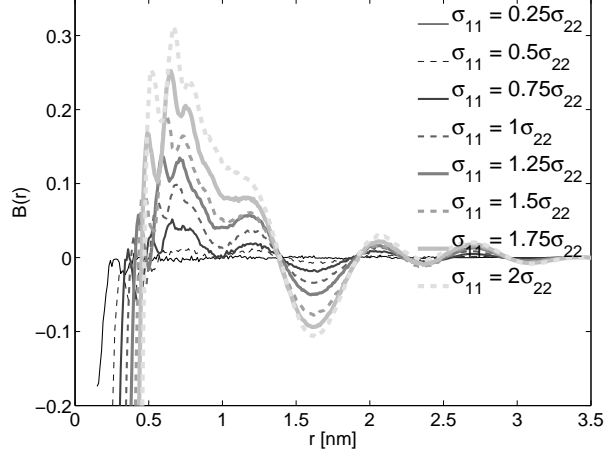


Figure 3: The bridge functionals B_{12} obtained from the MD simulations for the different solute/solvent size ratios (see equation (7))

The distance r_0 is chosen is such a way that $U_{12}(r_0) = 13.8k_B T$, where $U_{12}(r)$ is the solute-solvent LJ potential, k_B is the Boltzmann constant, T is the temperature. The parameters a_1 and a_2 were chosen to minimize the difference between the RDF obtained from the MD simulations and the RDF obtained using the closure relation:

$$a_1, a_2 = \text{argmin} ||g_{12}(r) - g_{\text{closure}}(a_1, a_2, r)|| \quad (9)$$

where $g_{\text{closure}}(a_1, a_2, r) = \exp(-\beta U_{12}(r) + g_{12}(r) - c_{12}(r) + B_{12}(a_1, a_2, r) - 1)$ and the norm is defined by the following expression:

$$||g_{12}(r) - g_{\text{closure}}(a_1, a_2, r)|| = \int_0^\infty (g_{12}(r) - g_{\text{closure}}(a_1, a_2, r))^2 dr \quad (10)$$

The coefficients a_1 and a_2 were parameterized as the functions from the solute/solvent size ratio: $a_1 = a_1(\sigma_{11}/\sigma_{22})$, $a_2 = a_2(\sigma_{11}/\sigma_{22})$. In such a way we obtain the effective bridge functional, which depends on one parameter - the solute/solvent size ratio.

$$B_{12}(\sigma_{11}/\sigma_{22}) = -a_1(\sigma_{11}/\sigma_{22}) \exp(-a_2(\sigma_{11}/\sigma_{22})(r - r_0)) \quad (11)$$

To check the effectiveness of the parameterization we compared the solutions of the Ornstein-Zernike equation with the hyper netted chain closure ($B_{12}(r) = 0$), the solutions of the OZ equation with the closure which includes the empirical bridge functional (11) and the results of the MD simulations. The Ornstein-Zernike equations were solved using the iterative algorithm. To do this the functions $\gamma_{12}(r) = h_{12}(r) - c_{12}(r)$ were introduced. The following algorithm was used: the first approximation was chosen to be $\gamma_{12}^{(0)}(r) = 0$. The $(n+1)$ -st approximation $\gamma_{12}^{(n+1)}(r)$ was obtained from the n -th approximation using the following algorithm[7]:

- Step 1: $c_{12}(r) = \exp(-\beta U_{12}(r) + \gamma_{12}^{(n)}(r) + B_{12}(r)) - \gamma_{12}(r) - 1$;
- Step 2: $\hat{c}_{12}(k) = \mathcal{F}[c_{12}(r)]$
- Step 3: $\hat{\gamma}_{12}^{(n+1)}(k) = \rho \hat{c}_{12}(k) \cdot \hat{h}_{22}(k)$
- Step 4: $\gamma_{12}^{(n+1)}(r) = \mathcal{F}^{-1}[\hat{\gamma}_{12}^{(n+1)}(k)]$

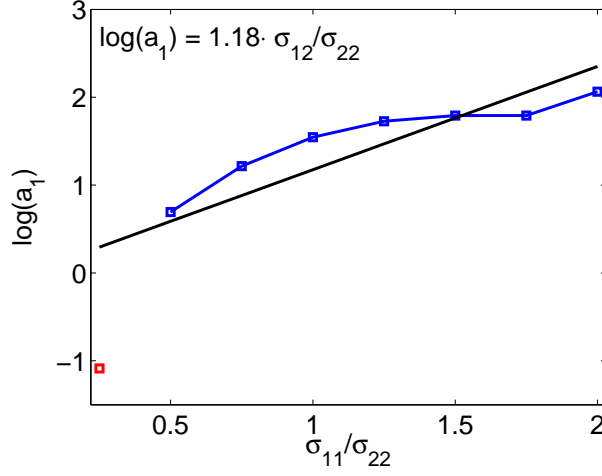


Figure 4: Dependence of the $\ln(a_1)$ on the solute/solvent size ratio

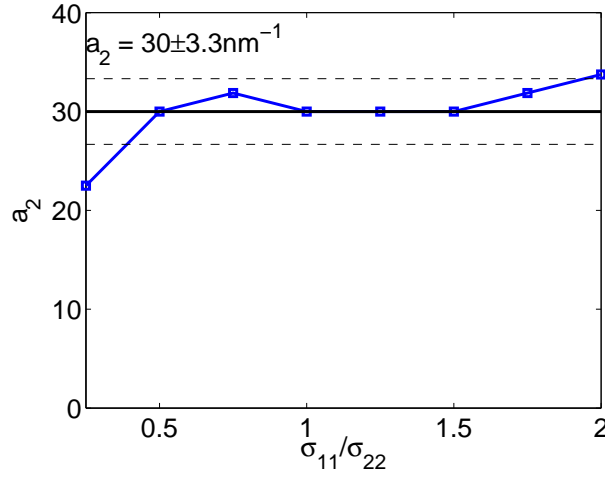


Figure 5: Dependence of the a_2 on the solute/solvent size ratio

3 Results

We performed the MD calculations for the infinitely diluted solutions of the LJ balls of diameter σ_{11} in the LJ fluid which consists of the balls of diameter σ_{22} . The following solute/solvent size ratios were used: $\sigma_{11}/\sigma_{22} = 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2$. From the MD simulation results the bridge functionals presented on the Figure 3 were obtained by using the expressions (4)- (7). For each ratio σ_{11}/σ_{22} the obtained bridge functional was fitted with the function (8) where coefficients a_1, a_2 were obtained as a result of solving the minimization problem (9).

In Figure 4 and Figure 5 one can see the dependencies of the coefficients a_1 and a_2 on the σ_{11}/σ_{22} ratio. As one can see in Figure 5, coefficient a_2 weakly depend on the σ_{11}/σ_{22} (standard deviation from the mean value is 3.3 nm^{-1} , while the mean value is 30 nm^{-1}). The coefficient a_2 can be approximated by its mean value: $a_2 \approx 30 \text{ nm}^{-1}$. Coefficient a_1 have an exponential dependence from the parameter σ_{11}/σ_{22} and thus $\ln(a_1)$ linearly depend on σ_{11}/σ_{22} . In Figure 4 for all σ_{11}/σ_{22} ratios from 0.5 to 2 the clear linear dependence of $\ln(a_1)$ on σ_{11}/σ_{22} is seen:

$$\ln(a_1) = C \cdot \sigma_{11}/\sigma_{22} \quad (12)$$

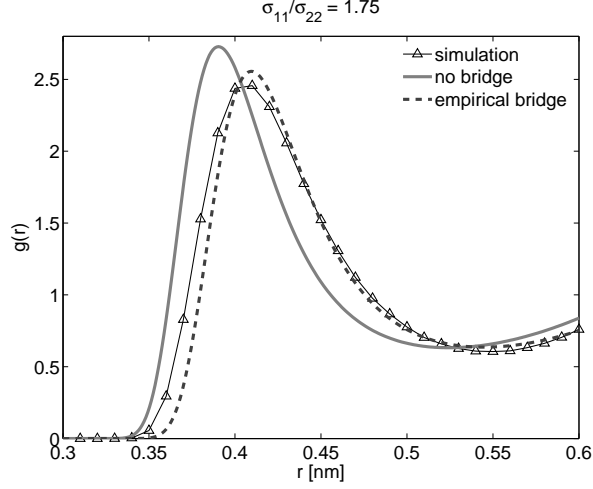


Figure 6: Comparison of the RDFs obtained from the Ornstein-Zernike equation with the closure without bridge functional and with the bridge empirical functional with the MD simulation results. $\sigma_{11}/\sigma_{22} = 1.75$

The exception is the ratio $\sigma_{11}/\sigma_{22} = 0.25$, which we do not use for the parameterization. For the values of a_1 , which correspond to the $\sigma_{11}/\sigma_{22} = 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2$ using the latest squares method the value of the C coefficient in the equation $\log(a_1) = C\sigma_{11}/\sigma_{22}$ as determined: $C = 1.1754$. In such a way, the final formula of the empirical bridge functional is the following:

$$B_{12}(\sigma_{11}/\sigma_{22}) = -\exp(-a_1(r - r_0) + C\sigma_{11}/\sigma_{22}) \quad (13)$$

where $a_1 = 30 \text{ nm}^{-1}$, $C = 1.1754$, $U_{12}(r_0) = 13.8k_B T$.

To check the empirical functional (13) for each of the ratios σ_{11}/σ_{22} we solve the Ornstein-Zernike equation with two different closures: hyper-netted chain, where the bridge functional $B_{12}(r) \equiv 0$, and with the closure, which includes the empirical functional built using the formula (13) (the $h_{22}(r)$ was taken from the MD simulation of the pure solvent). In Figure 6 the RDF obtained as a result of solving the OZ equation with the closure which includes the empirical bridge functional (13), the RDF obtained as a result of solving the OZ equation with the closure without the bridge functional and the results of the MD simulation are shown. The solute/solvent size ratio is $\sigma_{11}/\sigma_{22} = 1.75$. One can see, that the RDF, obtained without the bridge functional predicts incorrectly the position of the first peak of the RDF and also overestimate the height of the peak, while the RDF, obtained with the empirical bridge functional predicts correctly the position of the peak and more accurately predicts its height. In Table 1 the comparison of the first peak height obtained by using the different closures (with the bridge functional and without it) with the MD results is presented. One can see that both of the closures overestimate the height of the first peak of RDF, but in average the error of the closure with the bridge functional is 0.109, which is approximately 2.5 times lower than the error of the closure without the bridge. In Table 2 the comparison of the first peak position of RDF, obtained with the two different closures (with the bridge functional and without it) with the MD results is presented. One can see, that the closure without the bridge functional gives the systematic error of the first peak of RDF position around 0.01 nm (0.1Å), while the closure, which includes the bridge functional, determines the first peak position with the error which is 10 times lower (0.001 nm or 0.01Å). This error is negligible, because it is 10 times lower than the grid size which was used for the discretization of RDFs

σ_{11}/σ_{22}	peak height in MD	without the bridge functional		with the empirical bridge functional	
		peak height	difference from MD	peak height	difference from MD
0.25	1.853	1.943	0.090	1.831	-0.023
0.5	2.377	2.646	0.268	2.473	0.096
0.75	2.490	2.833	0.342	2.650	0.160
1	2.500	2.875	0.375	2.701	0.201
1.25	2.521	2.842	0.320	2.673	0.152
1.5	2.505	2.793	0.287	2.619	0.113
1.75	2.456	2.728	0.272	2.556	0.100
2	2.445	2.662	0.217	2.522	0.077
Average			0.272		0.109

Table 1: Comparison of the heights of the first peak of RDFs which were obtained by using the different closures with the MD simulations.

σ_{11}/σ_{22}	peak position in MD [nm]	without the bridge		with the empirical bridge	
		peak position [nm]	difference from MD [nm]	peak position [nm]	difference from MD [nm]
0.25	0.170	0.173	0.003	0.179	0.009
0.5	0.230	0.226	-0.004	0.230	0.000
0.75	0.280	0.268	-0.012	0.274	-0.006
1	0.310	0.304	-0.006	0.311	0.001
1.25	0.350	0.336	-0.014	0.345	-0.005
1.5	0.380	0.364	-0.016	0.378	-0.002
1.75	0.410	0.390	-0.020	0.409	-0.001
2	0.430	0.415	-0.015	0.437	0.007
Average			-0.011		0.001

Table 2: Comparison of the positions of the first peak of RDFs which was obtained using the different closures with the MD simulations.

obtained from the MD simulations. Additionally one need to stress the importance of the accurate approximations of the first peak position of the RDF for the solvation free energy calculations, because for that application small changes in the first peak position lead to the essential errors in the calculations.

4 Conclusions

In the paper the new universal bridge functional for the infinitely diluted solutions of the LJ spheres of different size in the LJ fluid is proposed. The investigated systems were the simplified model of the important case of aqueous solutions of different bioactive compounds. σ -parameter of the solvent LJ particles was chosen to be equal to σ parameter of the water oxygen in the SPC/E water model. The ratios of the solute/solvent particle sizes σ_{11}/σ_{22} was varying in the range from 0.25 to 2 which approximately corresponds to the distribution of the σ parameters of different atoms in the OPLS force-field.

For the mentioned above systems the MD simulations were performed. Using the RDFs, obtained from the MD simulations, and using the Ornstein-Zernike equation, the bridge functionals were obtained, which in turn were fitted by the exponential function (8), which depends on two parameters a_1 and a_2 .

Dependency of the parameters a_1 and a_2 on the σ_{11}/σ_{22} ratio was investigated. It was shown that the a_2 parameter weakly depends on the size of the solute, and for all of the investigated systems it can be put to be equal $a_2 = 30 \text{ nm}^{-1}$. It was shown that $\ln(a_1)$ correlates to the parameter σ_{11}/σ_{22} , and it can be estimated with a good accuracy using the formula (12). The final empirical bridge functional (13) was determined. This functional depends only on the solute/solvent particle size ratio.

Using the iterative algorithm the solutions of the Ornstein-Zernike equation for the closure with the empirical bridge functional were obtained. It was shown that introducing the bridge functional into the closure relation reduces by 2.5 times the error in the calculation of the first peak height of the RDF and, in contrast to the closure without the bridge, predicts accurately the position of the first peak of the RDF (with the error which is 10 times smaller than the grid discretization step). We have shown that introducing the empirical bridge functional into the closure relation can essentially improve the accuracy the predictions of the first peak of RDF position.

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